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A comparative Raman study between YbVO₃ and YVO₃

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Abstract. An orbital ordering effect is observed in YbVO₃ around 170 K while the crystal structure is orthorhombic (space group *pnma*). A monoclinic transition has been reported below $T_N = 104$ K, while according to recent specific heat measurements, it occurs at 170 K. The crystal structure of YVO₃ at 300 K is also orthorhombic. It becomes monoclinic at $T_c = 200$ K and back orthorhombic at $T = 77$ K. Spins order into the C-type antiferromagnetic structure below $T_{N1} = 116$ K and the order changes into the G-type antiferromagnetic structure below $T_{N2} = 77$ K. Controversial interpretations of YVO₃ Raman active excitations have been reported. For instance the 489 and 679 cm⁻¹ excitations have been assigned either to phonons or orbitons in two recent studies. In this communication we present a micro-Raman study of YbVO₃ and YVO₃ Raman active excitations as a function of temperature in order to trace the multiple phase transitions. Also by comparing the two single crystals spectra and previous studies in rare-earth manganites, high energy Raman active excitations are tentatively assigned.

1. Introduction

Recently, the experimental confirmation of a new kind of predicted elementary orbital wave excitations or orbitons [1] has represented a challenge for the condensed matter experimentalists. In transition metal oxides which are electron correlated Mott insulators, modulations in the relative shape of the electronic clouds in an orbitally ordered state could give rise to orbitons [2]. The orbitons represent a dynamical response that propagates between the lattice transition metal ion orbitals. They are considered as potential candidate for ultrafast switching using light electromagnetic field. First claim of orbiton detection was reported in a Raman scattering study of LaMnO₃ involving the exchange of O-2*p* and Mn-*eg* electrons [3]. Nevertheless, the assignment of these excitations to orbitons have been questioned [4-7]. Orbiton waves have also been investigated by infrared [8] and Raman scattering in YVO₃ a perovskite-type vanadium oxide; again controversial interpretations of the Raman active excitations have been reported [9, 10]. While Sugai and Hirota identified the 679 cm⁻¹ excitation as orbiton and the 489 cm⁻¹ excitation as phonon [9], Miyasaka et al. [10] reversed their identifications as phonon and orbiton respectively.

In the case of the RMnO₃ (R= Pr, Eu, Dy, Ho, Y) manganites, and based on polarization properties, lattice-dynamics calculation, and oxygen isotope substitution, Iliev et al. [7] have shown that all the

excitations attributed to orbitons by saito et al. [3] are pure phonons. In this communication we argue that the same situation prevails in high quality vanadates YVO_3 and YbVO_3 .

2. Experiment

0.5 cm^{-1} resolution Raman spectra were measured in the back-scattering configuration using a Labram-800 Raman microscope spectrometer equipped with a 50X ($\sim 0.35 \text{ mW}/(\mu\text{m})^2$; 3 μm laser spot) magnification objective, and a nitrogen cooled CCD detector. He:Ne ($\lambda = 6328 \text{ \AA}$ (1.96 eV)) laser, whose power was kept below 2 mW, and appropriate notch filter were used with the samples mounted on the cold finger of a micro-Helium Janis cryostat. Polycrystalline samples of $\text{Y}(\text{Yb})\text{VO}_3$ were prepared by the chemical reduction of $\text{Y}(\text{Yb})\text{VO}_4$ powder obtained by high-temperature solid-state reaction of stoichiometric mixtures of predried $\text{Y}(\text{Yb})_2\text{O}_3$ and V_2O_5 . $\text{Y}(\text{Yb})\text{VO}_4$ was reduced by annealing the powder in a flow of pure H_2 at 1000 °C. A single-crystalline boule of approximately 6mm in diameter and 60-70 mm in length was grown by traveling solvent floating zone method. The crystallinity of the boule was checked by X-ray and the composition by electron probe microanalysis.

3. Results and Discussion

The room temperature YVO_3 crystallographic structure is orthorhombic with $Pnma$ space group ($a = 5.61 \text{ \AA}$, $b = 7.55 \text{ \AA}$ and $c = 5.61 \text{ \AA}$). It becomes monoclinic ($P2_1/a$) at $T = 200 \text{ K}$ and undergoes two magnetic transitions at $T_{N1} = 116 \text{ K}$ and $T_{N2} = 77 \text{ K}$ [11]. The primitive cell contains four molecular units resulting in $7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$ Raman active modes.

A_g symmetry YVO_3 Raman active excitations as observed at 300 K ($\sim 266, 278, 337, 427, 475, 495 \text{ cm}^{-1}$) are shown in Fig. 1 as well as their temperature evolutions ($\sim 268, 279, 338, 429, 475, 500 \text{ cm}^{-1}$) at 80 K. A broad band ($650\text{-}750 \text{ cm}^{-1}$), not predicted by group analysis, is observed at 300K and is better resolved at 80 K ($\sim 650, 685, 705, 722 \text{ cm}^{-1}$).

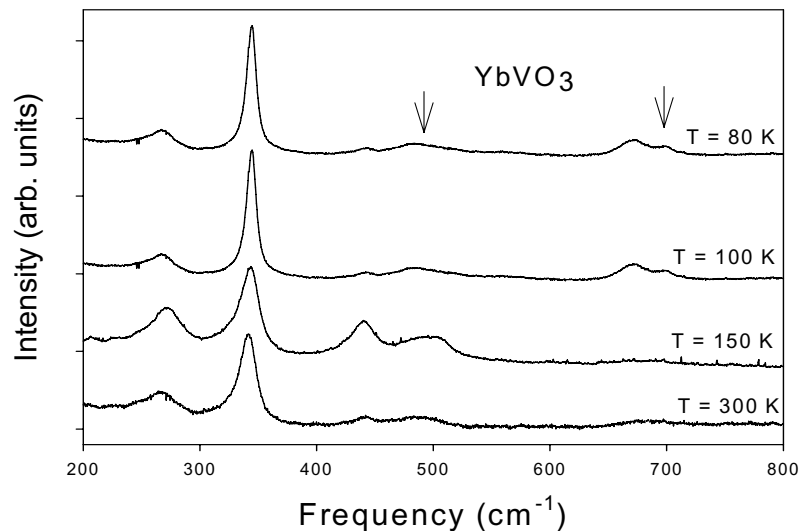


Figure 1. YVO_3 Raman active excitations as a function of temperature in the a(bb)a experimental configuration. Arrows indicate the excitations previously assigned to orbitons.

YbVO_3 vanadate is also orthorhombic, as YVO_3 , at room temperature and becomes magnetically ordered and monoclinic below $T_N = 104 \text{ K}$ [12] (however, recent unpublished specific heat measurements indicate that the monoclinic transition occurs at $T = 170 \text{ K}$). Its Raman active excitation frequencies are close to the ones of YVO_3 and have the same temperature evolutions as

shown in Fig. 2. ($\sim 253, 272, 544, 441, 486, 503 \text{ cm}^{-1}$) at 300 K and ($\sim 254, 272, 345, 442, 482, 516 \text{ cm}^{-1}$) at 80 K. Also similarly to YVO_3 , a broad band ($\sim 640\text{--}800 \text{ cm}^{-1}$) is observed at 300 K and resolved at 80 K ($\sim 653, 673, 694 \text{ cm}^{-1}$).

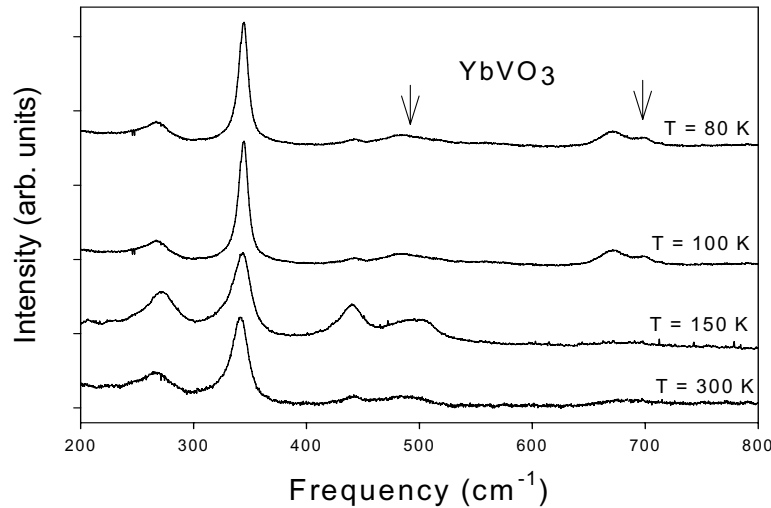


Figure 2. YbVO_3 Raman active excitations as a function of temperature in the a(bb)a experimental configuration. Arrows indicate the excitations previously assigned to orbitons.

In YVO_3 and YbVO_3 , the V^{3+} ion has two t_{2g} d electrons. One electron occupies the lower energy xy orbital and the other electron occupies either the yz or the xz orbital. While in YVO_3 the yz and xz orbitals order in the G-type below 200 K, and in the C-type below 77 K [11], in YbVO_3 important changes in the V-O distances are accompanied by reinforced orbital ordering below the magnetic transition at $T_N = 104 \text{ K}$ [12]. Interestingly, the excitations that have been designated in YVO_3 as orbitons around 700 cm^{-1} by one group [9] and 500 cm^{-1} by another group [10], are actually observed at room temperature in both YVO_3 and YbVO_3 vanadates at a temperature well above the orbital ordering temperatures for both compounds. Thus the 500 and 700 cm^{-1} excitations have phononic character. Nevertheless, as attested by their relative intensities with the A_g symmetry phonon 338 cm^{-1} (in YVO_3) or 345 cm^{-1} (in YbVO_3), their polarizabilities are affected by the various magnetic transitions and orbital orderings [13].

The detected excitations around 700 cm^{-1} outnumber the Γ point predicted phonons in the A_g symmetry. Moreover, they are not only observed in the A_g configuration but also in the b(ac)b configuration that corresponds to B_{1g} symmetry as shown in Fig. 3

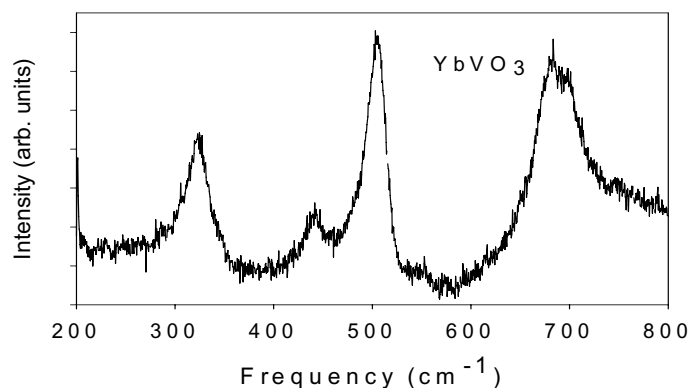


Figure 3. YbVO₃ Raman active excitations in the b(ac)b configuration at T = 80 K.

Similarly to the manganites which have the same structure and close frequency phonon excitations as vanadates, the excitations ($\sim 650, 685, 705, 722 \text{ cm}^{-1}$) in YVO₃ and ($\sim 653, 673, 694 \text{ cm}^{-1}$) in YbVO₃ could rather be of phonon density-of-states origin related to apex oxygens and plane oxygens as predicted by lattice dynamical calculations using a shell model [14]. Nature of these vibrations is further confirmed in the manganites by oxygen isotope substitution ($\text{O}^{16}/\text{O}^{18}$) that results in frequency-shifts proportional to the square root of the isotope mass [7]. Such result is consistent with phononic character and excludes orbiton character whose excitation frequency is not affected by oxygen substitution.

4. Conclusion

In this comparative Raman study of the YVO₃ and YbVO₃ single crystals, it is shown that all the Raman active excitations are of phonon origin solving an earlier controversy about their identifications. Their relative intensities are influenced by the various magnetic and orbital orderings that affect their polarizabilities as temperature is lowered. Similarly to the manganites, the excitations that are observed around 700 cm^{-1} at room temperature are associated with apex and plane oxygens [14] and assigned to some disorder induced phonon density-of-states.

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